

# **METAL POWDER AND POWDER MAGNETIC CORE USING THE SAME**

## **BACKGROUND OF THE INVENTION**

### **Field of Invention**

[0001] The present invention relates to a metal powder for a powder magnetic core using the metal powder. The present invention also relates to the powder magnetic core.

### **Description of Related Art**

[0002] In recent years, motor-driven electric controls have been widely used, such as, for instance, in various types of housing amenities, automobile power steering and power windows.

[0003] With regard to the above-mentioned usage, small-sized but high-power and well-controllable motors are generally required to be applied for these applications. This requirement is generally dictated by the limited space available.

[0004] Consequently, since general-purpose motors are sometimes difficult to use in these applications, there is a need to develop small-sized, high-performance motors.

[0005] When such new technology requiring smaller-sized motors is developed, it efficiently compressing into small size, will become very important because it greatly influences the performance of motors, without incurring any performance reduction.

[0006] In most of the conventional motors, a laminate core is used that is prepared by blanking out a laminate block with an electromagnetic steel or an iron sheet. The reason why such a laminate core is used is that the electromagnetic steel and the iron sheet are relatively inexpensive and possess good properties such as saturated magnetic flux density and magnetic permeability, which are essential for the motors.

[0007] However, a problem associated with reducing the size of the laminate is that production costs increase. Production costs increase because during blanking of laminate cores out of the original laminate block, the laminate block is required to have a specific size. Therefore, if the cores to be blanked out of the original laminate block are small in size, then the amount of the wasted part of the laminated block for the motor increases, after having been blanked. In addition, blanking smaller cores increases the probability of producing a larger number of faulty products. For example, when smaller cores are blanked out, a

considerable portion of them is capable of exhibiting defects such as burrs. As a result, it decreases the productivity of smaller cores.

[0008] Based on the above-mentioned problems, for the development of small-sized and high-performance motors, it would be desirable that a new core material, substitutable to the above-desired laminate cores, be developed.

[0009] Powder magnetic core, which is formed by filling a mold with ferromagnetic metal powder of iron, or the like, and molding it under pressure, becomes a viable alternative as a fine core material for motors.

[0010] The reason why such powder magnetic core is viable is described below. Compared with the laminate cores, powder magnetic cores do not generate any waste during their production. Therefore, powder magnetic cores present much cheaper production costs. In addition, since there is more freedom in designing the shape of the core, the design is able to be changed readily. For example, it would be possible to use the core in small-sized motors. Moreover, mixing the metal powder with an insulating material such as resin or inorganic powder increases the insulation performance of the metal powder for powder magnetic cores. So, the eddy current losses resulting from driving the motor are significantly reduced, and the motor efficiency therefore significantly increases. Such advantages cannot be obtained with laminate cores but can be obtained with powder magnetic cores.

[0011] Also, in case that such powder magnetic cores are actually used in motors, the powder magnetic cores needs to also exhibit improved properties.

[0012] First, the insulation performance of the powder magnetic core has to be high enough. When the magnetic field varies in time, such as may be the case inside of a motor, it is known that electromotive forces are generated inside the cores. Therefore, if the insulation performance of the cores is poor, then the electromotive forces generate eddy currents, which results in overheating the cores. The overheating of the cores is unfavorable since it significantly lowers the energy efficiency of the device and, in addition, may create substantial damage to the devices.

[0013] Therefore, the surface of iron powder is coated with an insulating substance in order to increase the insulation performance of the powder magnetic core itself.

[0014] Second, the magnetic properties of the powder magnetic core have to be sufficient. The magnetic flux density of conventional ordinary powder magnetic cores is lower than that of laminate cores. Therefore, when a powder magnetic core is used in a motor, it results in motor performance problems such as, for instance, lower torque.

Conventional powder magnetic cores do not exhibit a much lower insulation performance, but their magnetic flux density is generally insufficient to be used in motors.

[0015] Therefore, it is strongly desired to increase the magnetic flux density of the powder magnetic cores.

[0016] Accordingly, when powder magnetic cores are used in motors, the problems regarding insulation performance and magnetic flux density have to be solved.

[0017] As such, various methods for increasing the magnetic flux density and the insulation performance of the powder magnetic cores have been investigated so far.

[0018] It is known that the magnetic flux density of the powder magnetic cores increases with increasing the density of the compressed shaped articles of the powder magnetic cores. Based on such knowledge, various methods for increasing the magnetic flux density of the powder magnetic cores have been proposed.

[0019] One factor that causes the magnetic flux density to lower is the level of magnetic anisotropy of the cores, which depends on the morphology of the metal powder used in the cores. Regarding using the magnetic anisotropy, a method of reducing the magnetic anisotropy of the powder magnetic cores by flattening the particles of the magnetic powder to increase the magnetic flux density of the cores has been proposed (e.g., see patent reference 1).

[0020] However, according to this method, the particles that make up the metal powder inevitably develop morphological anisotropy, therefore having a high-magnetization axis and a low magnetization axis. Accordingly, the powder magnetic cores that are formed of such metal powder cannot be applied to motors and other devices where the magnetization direction varies.

[0021] In addition, the powder magnetic cores, formed by flattened particles alone, readily peel away in the machining direction of the flattened particles. Therefore, for increasing the strength of the compressed shaped articles of the powder, some amount of resin must be added. However, the resin added to the powder tends to lower the magnetic flux density of the powder magnetic cores and the fact that the additive resin decreases the magnetic flux density of the powder magnetic cores is an additional problem.

[0022] In addition, various methods have also been investigated to increase the insulation performance of the compressed shaped articles.

[0023] For example, methods to coat an iron powder with a resin binder, such as, for example, epoxy resin or fluororesin to increase the strength of the powder magnetic cores formed of the thus-coated powder (e.g., see patent reference 2) have been proposed.

[0024] The additive binder increases the insulation performance of the compressed shaped articles of powdery magnetic cores, but a problem arises in that it may significantly lower the magnetic flux density and the magnetic permeability of the cores, since the volume ratio of the iron to the powder magnetic cores decreases. Therefore, this method is not applicable to the motor cores that require high magnetic flux density.

[0025] In addition to the method of using a resin as mentioned above, methods of coating the surface of soft magnetic powder with a glassy insulating material that comprises indispensable elements of P, Mg, B and Fe to thereby increase the insulation performance of the thus-coated powder (e.g., see patent reference 5) have been proposed.

[0026] However, when the soft magnetic powder obtained according to the method is shaped under a high pressure equal to or greater than 588 MPa, then the glassy insulating material is broken and the insulation performance of the thus-shaped article becomes thereby significantly lowered. Therefore, the proposed method shows that increasing the density of the shaped article does not necessarily bring about an increase in the magnetic flux density thereof.

[0027] For increasing the insulation performance of metal powder without lowering the magnetic flux density thereof, another method comprises processing the surface of the metal powder with acid.

[0028] For example, P. Lefebver, et al. have reported that, when metal powder is processed on its surface with sulfuric acid to increase the surface roughness thereof, then the insulation performance of the thus-processed metal powder increases (e.g., see non-patent reference 1).

[0029] Further disclosed is a technology to use the iron powder coated with phosphoric acid on the surface to obtain powder magnetic cores which has an increased insulation performance (e.g., see patent reference 3 and patent reference 4).

[0030] The method for using sulfuric acid or phosphoric acid as mentioned above is effective for preventing any reduction of the density of the compressed shaped articles, since no resin is added to the articles. In this method, however, since acid is used for the surface treatment, a problem arises in that the acid that remains on the metal and that has not reacted with the metal gradually corrodes the metal. As a result, the magnetic properties and the

insulation performance of the powder magnetic cores formed by this method deteriorate with time. In addition, another problem arises in that the insulation performance of the powder magnetic cores, which is formed of the metal, is not enough.

[Patent Reference 1] JP-A 2-153003 (claims),

[Patent Reference 2] JP-A 59-50138 (claims),

[Non-patent Reference 1] P. Lefebver et al.; *Powder Met*, 1999, 42, pp. 325-330,

[Patent Reference 3] JP-A 7-245209 (claims),

[Patent Reference 4] JP-T 2000-504785 (claims) (the term "JP-T" as used herein means a published Japanese translation of a PCT patent application),

[Patent Reference 5] JP-A 6-260319 (claims).

## **SUMMARY OF THE INVENTION**

[0031] One of the advantages of the present invention is that it solves the above-described problems and one of its objects is to provide metal powder for powder magnetic cores which has the advantages of good insulation performance and high magnetic flux density, and which is usable in motor cores. Another object of this invention to provide a powder magnetic core formed by the metal powder.

[0032] In order to attain the objects mentioned above, the surface treatment of metal and metal powder was carefully studied.

[0033] As a result, it is found that, when the surface of a metal powder is processed with an aluminum-containing phosphate or phosphoric acid compound, a chemical reaction occurs on the surface of the thus-processed metal powder to form an insulating layer of improved adhesiveness. This insulating layer has the advantages, for instance, of improved impact resistance, pressure resistance and improved corrosion resistance.

[0034] In addition, it was further found that, even when the powder is shaped under a high pressure equal to or greater than 686 MPa, the insulating layer does not break and retains its good insulating performance.

On the basis of these findings, the present invention was conceived.

Some of the characteristics of this invention are as follows:

(1) Metal powder comprising:

a ferromagnetic metal powder;  
a coating material to coat a surface of the ferromagnetic metal powder; and  
a coated metal powder coated on the surface of the  
ferromagnetic metal powder with the coating material;  
wherein the coating material is a phosphoric acid compound which  
contains aluminum.

(2) The metal powder according to (1), wherein the ferromagnetic metal powder comprises at least one powder selected from the group consisting of iron powder, Fe-Si alloyed powder, Fe-Al alloyed powder, Fe-Ni alloyed powder, sendust powder and iron-based amorphous alloyed powder.

(3) The metal powder according to (1), wherein the phosphoric acid compound containing aluminum in the coating material satisfies the following formula:

$$1 \leq P/M \leq 10$$

wherein P (mol) indicates the phosphorus content of the coating material,  
and M (mol) indicates the overall metal content of the coating material.

(4) The metal powder according to (3), wherein the phosphoric acid compound containing aluminum in the coating material satisfies the following formula:

$$2 \leq P/M \leq 3$$

wherein P (mol) indicates the phosphorus content of the coating material,  
and M (mol) indicates the overall metal content of the coating material.

(5) The metal powder according to (1), wherein the number of moles of the phosphoric acid compound is in the range  $0.3 \leq \alpha \leq 1$ ,

wherein the number of moles of all the metal elements in the coating material is M, the number of moles of the aluminum element in the coating material is by  $\alpha M$  ( $0 \leq \alpha \leq 1$ ), and the number of moles of the metal component other than the aluminum elements in the coating material is  $(1-\alpha)M$ .

(6) The metal powder according to (1), wherein the phosphoric acid compound in the coating material comprises at least one selected from the group consisting of metaphosphoric

acid, pyrophosphoric acid, orthophosphoric acid, triphosphoric acid, tetraphosphoric acid, phosphoric acid monoesters, monomethylphosphoric acid, monoethylphosphoric acid, monophenylphosphoric acid, and their corresponding salts.

(7) The metal powder according to (1), wherein the metal compound containing aluminum in the coating material comprises at least one compound selected from the group consisting of aluminum oxide, aluminum nitrate, aluminum acetate, aluminum hydroxide, aluminum phosphate, and aluminum chloride.

(8) The metal powder according to (1), further comprising an organic resin.

(9) The metal powder according to (8), wherein the organic resin comprises at least one resin selected from the group consisting of epoxy resin, phenolic resin, silicone resin, amide resin and amide resin.

(10) The metal powder according to (1), further comprising an oxide.

(11) The metal powder according to (1), further comprising a surfactant and a silane compound.

(12) The metal powder according to (1), wherein the amount of the coating material to coat the surface of the metal powder is within a range of 0.01 to 5 mass % of the total amount of the metal powder.

(13) A powder magnetic core comprising:

a ferromagnetic metal powder;

a coating material to coat the surface of the ferromagnetic metal powder;

and,

a coated metal powder coated on the surface of the ferromagnetic metal powder with the coating material; and,

a powder magnetic core compacted by submitting the coated metal powder to pressure;

wherein the coating material is a phosphoric acid compound containing

aluminum.

(14) The powdery magnetic core according to (13), wherein the phosphoric acid compound, which contains aluminum in the coating material, satisfies the following:

$$1 \leq P/M \leq 10$$

wherein P (mol) indicates the phosphorus content of the coating material,  
and M (mol) indicates the overall metal content of the coating material.

(15) The powder magnetic core according to (13), wherein the phosphoric acid compound containing aluminum in the coating material satisfies the following:

$$2 \leq P/M \leq 3$$

wherein P (mol) indicates the phosphorus content of the coating material,  
and M (mol) indicates the overall metal content of the coating material.



## **DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS**

[0035] The invention is described in detail as follows.

[0036] The invention discloses a metal powder characterized by the fact that it is prepared by coating the surface of a starting powder of an essentially ferromagnetic metal such as iron (hereinafter referred to as "starting powder") with a phosphate or phosphoric acid compound containing aluminum, in which the material to coat the surface of the starting powder is prepared, for example, from a phosphoric acid compound and a metal compound containing aluminum.

[0037] In various exemplary embodiments, the term "phosphoric" acid compound used in the starting material for the coating material is a generic term for phosphoric acids which have at least 2 hydroxyl groups bonding to a phosphorus atom and which are obtained through hydration of diphosphorus pentoxide and their salts. Concretely, it may include metaphosphoric acid, pyrophosphoric acid, orthophosphoric acid, triphosphoric acid, tetraphosphoric acid and their salts. Apart from the above-mentioned acid, any other phosphoric acid compound is also employed in the invention, including, for example, phosphoric monoesters such as monomethylphosphoric acid, monoethylphosphoric acid, monophenylphosphoric acid, and still other phosphoric acids and their salts. In various exemplary embodiments, the phosphoric acid compounds are soluble in solvents such as water.

[0038] In various exemplary embodiments, the metal compound containing aluminum for the other starting material for the coating material may be any one that contains aluminum. In other exemplary embodiments, the aluminum-containing compounds can be aluminum oxides, phosphates, nitrates, acetates, hydroxides and chlorides.

[0039] In various exemplary embodiments, a metal compound that does not contain aluminum may be combined with a metal compound containing aluminum. For example, oxides, phosphates, carbonates, nitrates, acetates, hydroxides and chlorides of any of Mg, Mn, Zn, Co, Ti, Sn, Ni, Fe, Zr, Sr, Cu, Ca, V, Ba, etc. Additionally, in the invention, a non-metal element-containing compound may be combined with a metal compound. For example, oxides, phosphates, carbonates, nitrates, acetates, hydroxides and chlorides of any of Y, B, etc.

[0040] In various exemplary embodiments, these metal compounds are also soluble in solvents such as water for practicality.

[0041] In various exemplary embodiments, the phosphate or phosphorus acid compound containing aluminum that coats the surface of the starting powder in the invention is so designed that the molar ratio P/M is within a range of about 1 to 10, in which P (mol) indicates the phosphorus content of the coating material and M (mol) indicates the overall metal content of the coating material. The reason why such range is preferable in various exemplary embodiments is, when the ratio P/M is equal to or greater than 1, then the chemical reaction on the metal surface can take place and the adhesiveness of the chemical film to the surface of the metal powder increases. As a result, the strength and the insulation performance of the compressed shaped articles of the coated powder is further increased. In various exemplary embodiments, when the ratio P/M is smaller than about 10, then no free phosphoric acid remains on the coated metal powder. As a result, the metal powder does not corrode. In various exemplary embodiments, the ratio P/M falls within a range from about 1 to 5. In various exemplary embodiments, the ratio P/M is controlled to fall between about 2 and 3, so as to more effectively prevent the specific resistivity of the coated metal powder core from fluctuating and become unstable.

[0042] In order to control the ratio P/M, to fall within a defined range, for example, the following method may be used. In various exemplary embodiments, a method for suitably determining the amount of the phosphoric acid compound, the aluminum compound and the other metal compound to be mixed, so that the ratio P/M falls within a desired value. In various exemplary embodiments, there is a method of preparing the coating material with a predetermined ratio P/M by further adding any of the phosphoric acid compound, the aluminum compound and the other metal compound to the resulting mixture in order to achieve the desired value of P/M. The present invention discusses these methods, as well as other methods similar to in methodology and scope.

[0043] The ratio P/M may be defined, for example, as follows: The phosphorus content and the other metal content of the compound are determined through quantitative analysis, then they are converted into the molar ratio of the constitutive components. Alternatively, the phosphorus content and the other metal content of the starting materials are determined through quantitative analysis, and then the thus-determined starting materials are mixed in the desired molar ratio P/M.

[0044] In various exemplary embodiments, the method of quantitative analysis used to determine the ratio P/M comprises the following steps:

1) P and M in the coated iron powder and the starting powder are quantitatively determined. In this step, M is to include the constitutive components of the coating material.

2) The coating fraction of P and that of M are calculated as follows: (the content of the component in the coated powder) - (the content of the component in the starting powder).

3) The content of each element is divided by the atomic weight of P or M to give the molar content of each element.

4) From the molar content of each element obtained in the above, the ratio P/M is calculated.

[0045] In various exemplary embodiments, the coating film, or the lower or upper layer of the coating film may contain other substance than the aluminum-containing phosphate or phosphoric acid compound so far as the other substance does not have any negative influence on the magnetic flux density and other properties of the compressed shaped articles of the coated powder. The additional substance may include, for example, a material such as a surfactant for improving the wettability of the metal with the coating substance, a resin for binding the binding powder particles together, or any other additive for controlling the pH or other chemical or physical properties of phosphates or other coating substances used in coating the metal powder with the coating material. In various exemplary embodiments, the total content of the additional substance is not larger than 5 % by mass of the coating material.

[0046] In various exemplary embodiments, when the number of moles of all the metal elements in the coating film is indicated by M, the number of moles of the aluminum in the coating film is indicated by  $\alpha M$  ( $0 \leq \alpha \leq 1$ ) and the number of moles of the metal component other than aluminum is indicated by  $(1-\alpha) M$ , then  $\alpha$  is preferably from about 0.3 to about 1. This is because, when  $\alpha$  is greater than about 0.3, the amount of aluminum that is highly reactive with phosphoric acid is sufficient to eliminate any non-reacted free phosphoric acid and, as a result, the metal powder is protected from corrosion by the non-reacted phosphoric acid. In various exemplary embodiments, the range of the value  $\alpha$  is as follows: about  $0.4 \leq \alpha \leq$  about 1.0. Even more preferably, about  $0.8 \leq \alpha \leq$  about 1.0.

[0047] In various exemplary embodiments, the starting powder for use in the invention may be any metal powder that is ferromagnetic and that has a highly saturated magnetic flux density. The metal powder may include, for example, iron powder, Fe-Si alloyed powder such as typically Fe-3 % Si alloyed powder, as well as Fe-Al alloyed powder, Fe-Ni alloyed

powder, sendust powder, and iron-based amorphous alloy powder. In various exemplary embodiments, one or more different types of metal powder selected from these are used as the starting powder. In various exemplary embodiments, the starting powder may be pre-worked for shaping it more easily (for example, for shaping it into spherical granules).

[0048] In various exemplary embodiments, and with regard to the metal powder mentioned above, pure iron powder such as typically atomized iron powder, reduced iron powder and electrolytic iron powder are especially favorable for the starting powder of the invention. Because the magnetic properties of iron, such as saturated magnetic flux density and magnetic permeability, are good and, in addition, iron is easily compressible and is inexpensive. Examples of such pure iron powder are JFE Steel's KIP-MG270H and KIP-304AS.

[0049] In various exemplary embodiments, the particle size of the starting powder mentioned above is suitably determined depending on the use and the necessary properties of the powder magnetic cores that are formed as a result. In various exemplary embodiments, the constituent elements of the starting powder are controlled so as not to have any negative influence on the compressibility of the resulting powder and on the magnetic properties of the powder magnetic cores formed as a result.

[0050] In various exemplary embodiments, in order to form a coating film of phosphate or phosphoric acid compound containing aluminum for covering the surface of the starting powder, any method of vapor phase evaporation such as CVD or PVD can be used. In various exemplary embodiments, other dry coating treatment such as mechanofusion, or wet coating treatment can be effected by using a solution of the starting materials, phosphoric acid compound and metal compound. Any of these methods may be employed in the invention, as well as any other similar method. In various exemplary embodiments, the method of wet coating treatment with a solution of the starting materials, the phosphoric acid compound and the metal compound is especially good because of its simplicity, compared with, for instance, vapor phase evaporation. In the wet method, in addition, the blend ratio of the phosphoric acid compound and the aluminum compound may be readily controlled to fall within a desired ratio P/M. Therefore, the molar ratio P/M of phosphorus to metal elements is more accurately controlled, compared with, for instance, the dry coating treatment. Moreover, the wet method enables us to obtain more uniform coating of the surface of the starting powder with the coating material.

[0051] In various exemplary embodiments, in the wet coating treatment, it is desirable that the pH of the solution is controlled to fall within a desired range for the purpose of controlling the reactivity of the solution with metal. In various exemplary embodiments, the preferred pH range of the solution is in a range of about 1 to about 6. In various exemplary embodiments, when the pH of the solution is greater than 1, then the reactivity of the solution with metal is not too high, and while the starting powder is processed with the solution, starting powder does not react too much with the solution. As a result, the component and the composition of the coating film is uniform, and the adhesiveness thereof to the substrate increases. In various exemplary embodiments, when the pH value of the solution is smaller than about 6, then the reactivity of the solution is not too low,, and the solution forms a coating film in a good condition.

[0052] In various exemplary embodiments, for controlling the pH of the solution in the invention, a pH-controlling agent is added to the solution. The pH-controlling agent includes, for example, monosodium phosphate, disodium phosphate, sodium acid pyrophosphate, monopotassium phosphate, dipotassium phosphate, monosodium fumarate, and boric acid, or any other material than those mentioned above.

[0053] In various exemplary embodiments, for treating the starting powder in a wet condition, together with the solution, any method of stirring and mixing them in a tank stirrer such as an attritor or Henschel mixer may be acceptable. Otherwise, in various exemplary embodiments, there is a method of mixing them in a fluidized condition in a rotary fluidized-bed coating apparatus. Any of these methods or any other similar method is employed in the invention. In various exemplary embodiments, in order to treat the wet treatment therewith, the solution is applied to the metal powder all at once before or just after starting mixing them. In various exemplary embodiments, it is intermittently applied a few times to the powder while they are mixed. In various exemplary embodiments, the solution is continuously applied to the powder through a dropping device or a spray while the metal powder is mixed.

[0054] In various exemplary embodiments, spraying is favorable since it enables to uniformly apply the solution to the powder. In various exemplary embodiments, the spraying droplets of the solution has a reduced size of about 10  $\mu\text{m}$  or so, when the spraying condition is suitably controlled, and therefore, the coating film is prevented from becoming too thick. As a result, the metal powder is entirely coated with a uniform and thin coating film.

[0055] In various exemplary embodiments, when a fluidized-bed stirrer such as fluidized-bed granulator or rotary granulator or a stirring mixer such as Henschel mixer is used, an advantage is that the particles of the metal powder are prevented from aggregating. Accordingly, when the solution is sprayed onto the metal powder by using such a fluidized-bed stirrer or Henschel mixer, it allows the metal powder to be coated more uniformly. This is owing to the synergistic effect of the spraying operation and the action of the fluidized bed or the Henschel mixer. In various exemplary embodiments, in order to remove the solvent more rapidly and in order to promote the reaction further, it is advantageous to heat the system during or after mixing it.

[0056] In various exemplary embodiments, the amount of coating material to be applied to the metal powder is within a range from about 0.01 to about 5 % by mass of the metal powder. This is because, if the additive-coated amount is smaller than about 0.01 % by mass, then the metal powder may be unevenly coated because the amount of the coating material is too small and, as a result, the insulation performance of the coated powder becomes poor. In various exemplary embodiments, if the amount of coating material is larger than about 5 % by mass, then the proportion of the metal powder in the powder magnetic core decreases and the magnetic flux density of the core is thereby significantly lowered.

[0057] In various exemplary embodiments, when the starting powder is coated with the coating material to prepare the coated powder of the invention, the temperature of the starting powder and the coated powder is preferably lower than 110°C. During the coating process, if the temperature of the starting powder and the coated powder is greater than 110°C, then the insulation performance of the powder magnetic core formed of the coated powder becomes poor. In various exemplary embodiments, the temperature of the starting powder and the coated powder is lower than 100°C. In various exemplary embodiments, the temperature of the starting powder and the coated powder are not higher than 90°C. In order to ensure that the temperature of the starting powder and for the coated powder is lower than 110°C in the coating process, it is desirable that the temperature of the coating material and the atmosphere for the coating operation are also kept under 110°C.

[0058] In various exemplary embodiments, the lowermost limit of the temperature of the starting powder and the coated powder are not specifically defined, but they are set to be no lower than room temperature. In various exemplary embodiments, when the coating treatment is effected in a wet condition, for an example with water solvent, it takes a lot of time to remove the solvent if the working temperature is too low. And if so, the productivity

of the coated powder may decrease significantly. Therefore, the temperature is preferably not lower than 60°C, and in various exemplary embodiments not lower than 80°C. In various exemplary embodiments, not only the temperature of the starting powder and the coated powder, but also that of the coating operation atmosphere are preferably higher by at least 20°C than room temperature. In various exemplary embodiments, they are not lower than 60°C, and not lower than 80°C.

[0059] In various exemplary embodiments, during the process of coating the starting powder with the coating material for preparing the coated powder of the invention, the temperature of the starting powder and the coated powder may be controlled, for example, as follows: Hot air/cold air is directly applied to the starting powder and the coated powder to control the temperature of the powder; or the tank that contains the coated powder therein is heated/cooled at the intended temperatures. Any of these methods may be employed in the invention. The temperature of the starting powder and the coated powder may be controlled with any other similar method than those described herein. In various exemplary embodiments, in order to measure the powder temperature, for example any method for directly contacting the powder with a temperature sensor such as thermocouple can be used. In various exemplary embodiments, a method for monitoring the IR rays from the powder can also be used. In various exemplary embodiments, a method for monitoring the peripheral equipment and atmosphere, and for deriving the powder temperature by taking the related factors into consideration, such as thermal conductivity and convection can be used. Any of these methods or any other temperature measurement method can be used.

[0060] In various exemplary embodiments, in the metal powder of this invention, coated with a phosphate or phosphoric acid compound containing aluminum, unreacted free phosphoric acid remains present, although in a small amount, in the phosphate or the phosphoric acid compound. In various exemplary embodiments, the remaining free phosphoric acid makes the powder moisture-absorptive, and if the powder absorbs moisture, the phosphate or the phosphoric acid compound in the surface of the coating film may become denatured. As a result, the coating film shrinks, peels or softens. The specific resistivity of the powder magnetic core of this invention, formed by pressing the metal powder fluctuates and becomes unstable. Therefore, in various exemplary embodiments of this invention, it is desirable to process the coated powder for resistance to moisture absorption.

[0061] In various exemplary embodiments, the methods for making the coated powder resistant to moisture absorption may be any method of heating the metal powder being coated or the coated powder to thereby promote the crosslinking reaction between free phosphoric acid and aluminum, so as to remove the free phosphoric acid, or a method of coating the surface of the metal powder with a non-absorptive material to thereby make the thus-coated metal powder resistant to moisture absorption. Any other similar method may also be employed in this invention.

[0062] In various exemplary embodiments, in case that the metal powder is heated for making it resistant to moisture absorption, the heating temperature is preferably set in the range of 50°C to about 500°C. This is because, if the heating temperature is lower than about 50°C, it is too low to generate any crosslinking reaction. Additionally, the metal powder is not completely resistant to moisture absorption. On the other hand, if the heating temperature is higher than about 500°C, the thermal stress caused by the difference in the thermal expansion coefficient between the metal and the coating material increases and the coating material may be broken or may peel. The heating time is suitably determined depending on the used heating device and the amount of the powder to be processed. From the standpoint, of the production costs, in various exemplary embodiments, it is desirable that the temperature is from about 70 to 350°C and the heating time from about 10~60 minutes. In various exemplary embodiments, air is preferred as the atmosphere for the heating treatment, since it is easy to prepare and handle, and since heating does not significantly increase the production costs. In various exemplary embodiments, the atmosphere is preferably so conditioned that its relative humidity is at most about 40 % in order for the powder to be treated without absorbing any moisture from the atmosphere. In various exemplary embodiments, a method of heating the powder in a drier can be used because it is simple. Any other device and method such as rotary kiln, fluidized-bed drier can also be used.

[0063] In various exemplary embodiments, when the powder is subjected to treating for moisture absorption resistance as above, it is desirable that the ratio P/M is controlled to fall between about 2 and 3 because not only it can be done at low cost, but also the specific resistivity of the processed powder core becomes more effective because it becomes more stable.

[0064] In various exemplary embodiments, in order to coat the powder with a non-absorptive material for making it resistant to moisture absorption, for example, any method of coating the powder with an organic substance such as resin can be used. In various exemplary



embodiments, a method of coating the powder with an oxide such as silica, or a method of coating the powder with a monomolecular film of surfactant or silane compound can be used.

[0065] In various exemplary embodiments, when the powder is coated with an organic substance, for example, the organic substance can be any substance capable of forming a water-resistant film, such as a resin or any other organic substance. The resin may be, for example, epoxy resin, phenolic resin, silicone resin, amide resin, and imide resin or any other material.

[0066] In various exemplary embodiments, when the powder is coated with an oxide, for example, the oxide is selected from oxides of Ti, Zr, Si, Al, Y, or can be used in the invention so far as it is effective for moisture absorption resistance. In various exemplary embodiments, in order to coat the metal powder with the oxide, for example, any method of dipping the metal powder in an oxide precursor such as alcoxide compound, or coating the metal powder with such an oxide precursor, or a method of coating it with a colloidal oxide, or a method of coating it with plasma of oxide molecules can be used. Any other similar method to those described herein may also be employed in the invention.

[0067] In various exemplary embodiments, the alcoxide compound can be, for example, a metal alcoxide compound such as titanium alcoxide, zirconium alcoxide, aluminum alcoxide, silicon alcoxide. Of those alcoxide compounds, in various exemplary embodiments, silicon alcoxide is preferred, as it is easy to handle and is inexpensive. In various exemplary embodiments, for the alcoxide compound, alkyl silicates such as ethyl silicate and methyl silicate, and silane compounds are also preferred.

[0068] In various exemplary embodiments, the colloidal oxide includes, for example, alumina sol, silica sol, titania sol and zirconia sol. The solvent for dispersing the colloid may be any solvent, but water is preferred as it is easy to handle. In various exemplary embodiments, the particle size of the colloidal oxide may be any one as long as the oxide is dispersible. In various exemplary embodiments, in view of its influence on the compressibility of the coated powder into powder magnetic cores, the mean particle size of the oxide is preferably at most 0.1  $\mu\text{m}$ .

[0069] In various exemplary embodiments, when the powder is coated with a monomolecular film, a surfactant or a silane compound may be used for it. Any other similar material may also be used in the invention in order to attain the above-mentioned object.

[0070] In various exemplary embodiments, the surfactant includes, for example, nonionic surfactants such as polyoxyethylene alkyl ethers, polyoxyalkylene alkyl ethers,

polyoxyethylene derivatives, sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid esters, glycerin fatty acid esters, polyoxyethylene fatty acid esters, polyoxyethylene hardened castor oil, polyoxyethylene alkylamines, alkylalkanolamides, polyoxyethylene-polyoxypropylene condensates, polyoxyethylene-polyoxypropylene block polymers and ionic surfactants such as alkylsulfate ester salts, polyoxyethylene alkyl ether sulfate ester salts, sulfonic acid salts such as alkylbenzenesulfonic acid salts, fatty acid salts, alkylamine salts, and quaternary ammonium salts may also be used in this invention.

[0071] In various exemplary embodiments, the silane compound includes, for example, alkoxysilanes of which the silicon atom is terminated with a methyl group, methoxysilane, or with an ethyl group, ethoxysilane; alkylsilanes prepared by adding an alkyl group such as methyl or phenyl group to alkoxysilanes; and silane coupling agents prepared by adding an organic functional group such as amino, methacryl, vinyl, epoxy or mercapto group to the terminal of alkylsilanes. Any of these may be used in the invention, but, in various exemplary embodiments, silane-coupling agents are preferred. In various exemplary embodiments, aminosilane coupling agents having an amino group at the terminal thereof are preferred, since the amino group moiety may selectively react with free phosphoric acid, and therefore the ability of the agents to block free phosphoric acid is high, and, in addition, since the agent molecules themselves are highly repellent to water, the ability of the agents to resist moisture absorption is higher than that of the other alkyl group-having silane coupling agents.

[0072] In various exemplary embodiments, the above-mentioned materials may be mixed with the aluminum-containing phosphate or phosphoric acid compound or its aqueous solution, or they may be applied to the powder coated with the phosphate or phosphoric acid compound. When they are mixed with the aluminum-containing phosphate or phosphoric acid compound, they may react with the phosphate or phosphoric acid compound and the phosphate or phosphoric acid compound may become denatured. In particular, ionic surfactants and aminosilane coupling agents capable of forming ions in their aqueous solution may readily denature the phosphate or phosphoric acid compound owing to the action of the ions in the additives. Accordingly, in various exemplary embodiments, when such materials are used, it is desirable that the powder is first coated with the phosphate or phosphoric acid compound and then it is further coated with the additive in a separate step. When the powder coated with the phosphate or phosphoric acid compound is further coated with the moisture-resistant material in a separate step, then the material separately added to the powder for moisture absorption resistance may more effectively cover the whole of the metal powder.

Therefore, the method is more favorable as it is more effective for water absorption resistance.

[0073] In various exemplary embodiments, the amount of the moisture absorbing material to be added to the metal powder is at least about 0.01 % by mass but at most about 2.0 % by mass of the metal powder. This is because if it is smaller than about 0.01 % by mass, the material cannot fully perform its moisture absorbing properties; but if the amount of moisture-absorbing material is larger than about 2.0 % by mass, it may lower the compressibility of the metal powder and, as a result, the magnetic flux density of the powder magnetic core formed of the powder and the strength of the part may decrease. In various exemplary embodiments, the amount of the material to be added is from about 0.01 % by mass to about 1.5 % by mass, and, in various exemplary embodiments from about 0.01 % by mass to about 1.0 % by mass.

[0074] In various exemplary embodiments, to add the moisture-resistant material to the metal powder, any method can be used. However, in various exemplary embodiments, a wet treatment with a solution of the moisture-resistant material like that for the case of coating the powder with the aluminum-containing phosphate or phosphoric acid compound is preferred, since the powder may be uniformly applied to the entirety of the powder in such wet treatment. In particular, is, in various exemplary embodiments, a method of spraying the material on the powder, is preferred since the coating material may be more uniformly applied to the powder in the method and since controlling the spraying condition controls the film condition. Any other similar method for adding the moisture-resistant material to the metal powder can be used.

[0075] In various exemplary embodiments, during or after coating with the moisture-resistant material, the metal powder may be heated for removing the solvent and for thermally curing and stabilizing the moisture-resistant material. The heating condition may be suitably determined depending on the material used.

[0076] In various exemplary embodiments, the surface-coated metal powder may be molded under pressure in a mold.

[0077] In various exemplary embodiments, the molding pressure may be suitably determined depending on the use of the molded articles. In various exemplary embodiments, increasing the molding pressure is preferred since it may increase the green density of the molded articles, therefore bettering the magnetic properties such as magnetic flux density thereof and further increasing the mechanical strength of the molded articles. In various

exemplary embodiments, the molding pressure is at least about 490 MPa, and, in various exemplary embodiments, at least about 980 MPa.

[0078] In various exemplary embodiments, a lubricant may be applied or added to the entire surface of the mold in which the coated metal powder is molded. The lubricant is effective for reducing the friction between the mold and the powder molded therein under pressure, and is therefore effective for preventing the reduction in the density of the molded articles. In addition, the lubricant further reduces the friction of the molded articles when they are taken out of the mold, and is therefore effective in preventing the molded articles from being cracked or damaged while they are taken out of the mold.

[0079] In various exemplary embodiments, the lubricant includes, for examples, metal soap such as lithium stearate, zinc stearate or calcium stearate, and wax such as fatty acid amides.

[0080] In various exemplary embodiments, the powder magnetic core that is formed of the metal powder obtained according to the invention may be subjected to heat treatment, after its formation through pressure molding, for strain removal from it to thereby reduce the hysteresis loss thereof. The heat treatment condition including the heating temperature, the heating time and the heating atmosphere may be suitably determined in accordance with the use of the product. In various exemplary embodiments, the heating temperature may be set between about 300 and 700°C, and the heating time may be set between about 5 and 120 minutes. In various exemplary embodiments, the heating atmosphere may be air in which the powder may be processed in a simple heating device, or an inert atmosphere such as Ar or N<sub>2</sub>, or a reducing atmosphere such as H<sub>2</sub>, or in vacuum. The dew point of the atmosphere may be suitably determined in accordance with the use of the product. During the heat treatment, or during the step of heating or cooling it, the product may be kept at a constant temperature for a predetermined period of time.

[0081] The compressed shaped articles thus formed in the manner as described above have a high magnetic flux density and good insulation performance, and are free from the corrosion that is generally problematic in treatment with acid.

[0082] In various exemplary embodiments, when the temperature of the starting powder and the coated powder of the invention is kept under 110°C during the process of producing the coated powder by coating the starting powder with a coating material, then the insulation performance of the powder magnetic core formed of the coated powder is better. It is known that, when the aluminum-containing phosphate compound is heated, it undergoes various

physical changes and, in particular, when it is heated from room temperature up to 110°C, it undergoes phase transformation into a readily-hydrolyzable unstable condition (\*1). The temperature control in coating the starting powder under 110°C in the present invention could prevent the phase transformation and could therefore have some positive influence on improving the insulation performance of the coated powder.

(\*1) Mitsutomo Tsuwako, *Inorganic Polymer*, CMC (1985), pp. 265-266.

Examples of the invention are described below.

#### Example 1:

[0083] Iron powder KIP-304AS (by JFE Steel) was used for the starting powder. For the coating material, used was a mixture of phosphoric acid compound and metal compound that had been conditioned to have a ratio P/M (by mole) as in Table 1 below. For the ratio P/M, the data were rounded off at the tenth place thereof.

[0084] The powder was coated in wet treatment. The solution for the wet treatment had a solid concentration of 5 % by mass in distilled water.

[0085] For controlling the ratio P/M, the dissolution ratio or the blend ratio of the phosphoric acid compound and the metal compound was controlled, or the phosphate was dissolved in the solution so as to have a predetermined ratio P/M. The ratio P/M was so controlled that the molar ratio,  $\alpha$ , of the aluminum atom to all the metal components could be  $0 < \alpha \leq 1$ . To samples 26 to 30 of the invention, added was the pH-controlling agent as in Table 1 for their pH control.

[0086] A rotary fluidized-bed coating apparatus was used for mixing the coating material and the starting powder. While the starting powder was fluidized in the apparatus, the coating material was sprayed on the fluidized powder in such a controlled manner that the solid content of the coating material could be as in Table 1. After being sprayed, the powder was kept fluidized for 20 minutes and dried. Through the treatment, the metal powder was coated with the coating material on the surface of the starting powder. The tank temperature, the starting material temperature and the coated powder temperature were all 80°C. Up to 0.2 % by mass of a lubricant, zinc stearate was added to the powder, which was then pressed in a mold into a ring sample (outer diameter, 38 mm; inner diameter, 25 mm; height 6.2 mm). The molding pressure was between 980 and 1980 MPa. When no lubricant was added to the powder, a lubricant dispersion solution prepared by dispersing zinc stearate in water was applied to the inner wall of the mold for mold lubrication. Some of the thus-molded ring

samples were heated in air at 400°C for 60 minutes. The amount of the lubricant added to the powder, the molding pressure, and the presence or absence of heat treatment of the ring samples is shown in Table 2.

[0087] The green density, the specific resistivity and the magnetic flux density of the thus-molded ring samples were measured, and the data are given in Table 2.

[0088] The size and the weight of each sample were measured, and the green density thereof was computed from the data. The specific resistivity was measured according to a four-terminal method in which the current was 1 A. The magnetic flux density was measured as follows: A formal enamelled wire of 0.6 mm in diameter was wound around the ring sample, with 100 turns on the primary side and 20 turns on the secondary side. The resulting coil was tested for the magnetic flux density  $B_{10k}$  thereof in a magnetic field  $H = 10 \text{ kA/m}$ .

[0089] To check the samples as to whether or not their resistivity and magnetic properties may worsen in time, the samples were stored at a temperature of 25°C and a humidity of 40 % for 10 days, and their specific resistivity and magnetic flux density were measured in the same manner as above.

[0090] The solid content is hereinafter defined as follows: The solvent is evaporated away from the coating material, which is sprayed to the metal powder, and the amount of the remaining solute is measured.

Table 1

No.	Phosphoric Acid Compound designation	Metal Compound 1		Metal Compound 2 (or pH-controlling agent)		P/M	$\alpha$	pH	Solid Content	Remarks
		designation	ratio*	name	ratio*					
1	85 % orthophosphoric acid	aluminum hydroxide	100	-	-	2	1	1.2	0.20	sample 1 of the invention
2	85 % orthophosphoric acid	aluminum hydroxide	100	-	-	10	1	2.0	0.50	sample 2 of the invention
3	85 % orthophosphoric acid	aluminum hydroxide	100	-	-	4	1	1.2	1.00	sample 3 of the invention
4	85 % orthophosphoric acid	aluminum chloride	100	-	-	2	1	1.0	0.10	sample 4 of the invention
5	85 % orthophosphoric acid	aluminum chloride	100	-	-	2	1	1.0	0.20	sample 5 of the invention
6	85 % orthophosphoric acid	aluminum chloride	100	-	-	2	1	1.0	0.20	sample 6 of the invention
7	85 % orthophosphoric acid	aluminum chloride	100	-	-	4	1	1.0	0.50	sample 7 of the invention
8	85 % orthophosphoric acid	aluminum chloride	100	-	-	6	1	1.0	1.00	sample 8 of the invention
9	85 % orthophosphoric acid	aluminum acetate	100	-	-	2	1	1.0	0.10	sample 9 of the invention
10	85 % orthophosphoric acid	aluminum acetate	100	-	-	2	1	1.2	0.20	sample 10 of the invention

No.	Phosphoric Acid Compound	Metal Compound 1		Metal Compound 2 (or pH-controlling agent)		P/M	$\alpha$	pH	Solid Content	Remarks
		designation	ratio*	name	ratio*					
11	85 % orthophosphoric acid	aluminum acetate	100	-	-	3	1	1.2	1.00	sample 11 of the invention
12	85 % orthophosphoric acid	aluminum acetate	100	-	-	3	1	1.2	3.00	sample 12 of the invention
13	85 % orthophosphoric acid	aluminum acetate	100	-	-	7	1	1.2	5.00	sample 13 of the invention
14	-	aluminum phosphate	100	-	-	1	1	1.2	0.05	sample 14 of the invention
15	-	aluminum phosphate	100	-	-	2	1	1.2	0.10	sample 15 of the invention
16	-	aluminum phosphate	100	-	-	3	1	1.2	0.05	sample 16 of the invention
17	-	aluminum phosphate	100	-	-	3	1	1.2	0.10	sample 17 of the invention
18	-	aluminum phosphate	100	-	-	3	1	1.2	0.20	sample 18 of the invention
19	-	aluminum phosphate	100	-	-	3	1	1.2	0.50	sample 19 of the invention
20	-	aluminum phosphate	100	-	-	4	1	1.2	1.00	sample 20 of the invention
21	pyrophosphoric acid	aluminum acetate	100	-	-	2	1	1.5	1.00	sample 21 of the invention
22	85 % orthophosphoric acid	aluminum hydroxide	50	manganese phosphate	50	2	0.5	3.0	0.50	sample 22 of the invention
23	-	aluminum phosphate	80	zinc nitrate	20	4	0.2	1.5	0.75	sample 23 of the invention



No.	Phosphoric Acid Compound	Metal Compound 1		Metal Compound 2 (or pH-controlling agent)		P/M	$\alpha$	pH	Solid Content	Remarks
		designation	ratio*	name	ratio*					
24	designation	aluminum phosphate	100	-	-	3	1	1.2	0.20	sample 24 of the invention
25	-	aluminum phosphate	100	-	-	3	1	1.2	0.20	sample 25 of the invention
26	-	aluminum phosphate	90	monosodium fumarate	10	3	0.9	3.0	0.10	sample 26 of the invention
27	-	aluminum phosphate	90	sodium acid pyrophosphate	10	3	0.9	4.0	0.10	sample 27 of the invention
28	-	aluminum phosphate	90	monopotassium phosphate	10	3	0.9	4.0	0.10	sample 28 of the invention
29	-	aluminum phosphate	90	boric acid	10	3	1	4.0	0.10	sample 29 of the invention
30	-	aluminum phosphate	80	boric acid	20	3	1	6.0	0.10	sample 30 of the invention
31	-							-	-	comparative sample 1
32	-							-	-	comparative sample 2
33	epoxy resin							-	0.20	comparative sample 3
34	epoxy resin							-	0.50	comparative sample 4
35	epoxy resin							-	1.00	comparative sample 5
36	0.1 N sulfuric acid							0.1	0.20	comparative sample 6
37	85 % orthophosphoric acid							0.8	0.20	comparative sample 7

No.	Phosphoric Acid Compound	Metal Compound 1		Metal Compound 2 (or pH-controlling agent)		P/M	$\alpha$	Solid Content	Remarks
	designation	designation	ratio*	name	ratio*				
38	85 % orthophosphoric acid	163 g, MgO 31 g, boric acid 30 g					3.0	0.20	comparative sample 8
39	85 % orthophosphoric acid	163 g, MgO 31 g, boric acid 30 g					3.0	0.50	comparative sample 9
40	polyamide resin						-	1.00	comparative sample 10

\* Ratio: This is the ratio of the metal element atom of the indicated component to the number of atoms M of all the metal components.

Table 2

No.	Amount Added	Lubricant (mas.%)	Molding Pressure (MPa)	Heat Treatment	immediately after preparation			after 10 days		Remarks
					Green Density (Mg/m <sup>3</sup> )	Specific resistivity (μΩm)	Magnetic Flux Density B10k (T)	Specific resistivity (μΩm)	Magnetic Flux Density B10k (T)	
1	0.20	0.20	980	yes	7.54	95	1.50	100	1.50	sample 1 of the invention
2	0.50	0.20	980	yes	7.50	240	1.51	212	1.47	sample 2 of the invention
3	1.00	mold lubrication	980	no	7.35	4550	1.41	4479	1.41	sample 3 of the invention
4	0.10	mold lubrication	980	no	7.62	132	1.52	130	1.54	sample 4 of the invention
5	0.20	mold lubrication	980	no	7.59	242	1.50	244	1.51	sample 5 of the invention
6	0.20	mold lubrication	980	no	7.58	253	1.50	261	1.50	sample 6 of the invention
7	0.50	mold lubrication	1470	no	7.67	343	1.57	341	1.59	sample 7 of the invention
8	1.00	mold lubrication	1470	no	7.56	323	1.49	301	1.46	sample 8 of the invention
9	0.10	mold lubrication	1470	yes	7.73	98	1.69	101	1.70	sample 9 of the invention
10	0.20	mold lubrication	980	yes	7.64	103	1.57	105	1.58	sample 10 of the invention
11	1.00	mold lubrication	980	yes	7.45	1304	1.48	1381	1.48	sample 11 of the invention
12	3.00	mold lubrication	980	yes	7.23	8750	1.32	8749	1.34	sample 12 of the invention
13	5.00	mold lubrication	980	yes	7.01	12353	1.30	10579	1.27	sample 13 of the invention
14	0.05	0.20	980	no	7.64	85	1.63	89	1.64	sample 14 of the invention

No.	Amount Added	Lubricant (mas.%)	Molding Pressure (MPa)	Heat Treatment	immediately after pereparation				after 10 days		Remarks
					Green Density (Mg/m <sup>3</sup> )	Specific resistivity (μΩm)	Magnetic Flux Density B10k (T)	Specific resistivity (μΩm)	Magnetic Flux Density B10k (T)		
15	0.10	0.20	980	no	7.62	120	1.60	119	1.61	sample 15 of the invention	
16	0.05	mold lubrication	980	no	7.62	108	1.62	110	1.66	sample 16 of the invention	
17	0.10	mold lubrication	980	no	7.61	160	1.65	161	1.65	sample 17 of the invention	
18	0.20	mold lubrication	980	yes	7.62	200	1.63	203	1.64	sample 18 of the invention	
19	0.50	mold lubrication	1470	yes	7.65	398	1.58	401	1.59	sample 19 of the invention	
20	1.00	mold lubrication	1470	yes	7.54	1574	1.54	1575	1.53	sample 20 of the invention	
21	1.00	mold lubrication	1470	no	7.55	1245	1.55	1246	1.55	sample 21 of the invention	
22	0.50	mold lubrication	1980	no	7.75	308	1.73	310	1.73	sample 22 of the invention	
23	0.75	mold lubrication	980	yes	7.56	340	1.51	342	1.51	sample 23 of the invention	
24	0.20	mold lubrication	1980	yes	7.74	120	1.74	122	1.73	sample 24 of the invention	
25	0.20	mold lubrication	980	no	7.60	320	1.60	321	1.61	sample 25 of the invention	

No.	Amount Added	Lubricant (mas.%)	Molding Pressure (MPa)	Heat Treatment	immediately after pereparation				after 10 days		Remarks
					Green Density (Mg/m <sup>3</sup> )	Specific resistivity (μΩm)	Magnetic Flux Density B10k (T)	Specific resistivity (μΩm)	Magnetic Flux Density B10k (T)		
26	0.20	mold lubrication	980	no	7.60	520	1.60	520	1.61	sample 26 of the invention	
27	0.20	mold lubrication	980	no	7.61	542	1.59	542	1.60	sample 27 of the invention	
28	0.20	mold lubrication	980	no	7.60	453	1.59	454	1.60	sample 28 of the invention	
29	0.20	mold lubrication	980	no	7.62	592	1.61	593	1.61	sample 29 of the invention	
30	0.20	mold lubrication	980	no	7.62	493	1.61	495	1.62	sample 30 of the invention	
31	0.00	mold lubrication	980	no	7.66	8.5	1.67	8.0	1.68	comparative sample 1	
32	0.00	mold lubrication	1470	no	7.71	4.2	1.72	4.2	1.71	comparative sample 2	
33	0.20	mold lubrication	980	no	7.57	2310	1.54	2308	1.54	comparative sample 3	
34	0.50	mold lubrication	980	no	7.45	8710	1.48	8709	1.48	comparative sample 4	
35	1.00	mold lubrication	980	no	7.32	23600	1.35	23590	1.36	comparative sample 5	
36	0.20	mold lubrication	980	no	7.58	67	1.55	31	1.32	comparative sample 6	
37	0.20	mold lubrication	980	no	7.57	45	1.56	17	1.24	comparative sample 7	
38	0.20	mold lubrication	980	yes	7.62	24	1.59	16	1.60	comparative sample 8	

No.	Amount Added	Lubricant (mas. %)	Molding Pressure (MPa)	Heat Treatment	immediately after pereparation				after 10 days		Remarks
					Green Density (Mg/m <sup>3</sup> )	Specific resistivity (μΩm)	Magnetic Flux Density B10k (T)	Specific resistivity (μΩm)	Magnetic Flux Density B10k (T)		
39	0.50	mold lubrication	1470	yes	7.60	35	1.56	19	1.57	comparative sample 9	
40	2.00	mold lubrication	1470	*	6.80	14210	1.01	14200	1.00	comparative sample 10	

\* Heat treatment at 200°C for 2 hours.

[0091] As is obvious from Table 2, the samples of the invention all have high green density, high specific resistivity and high magnetic flux density, and their resistivity and magnetic properties did not lower at all in time. When sample 25 of the invention is compared with samples 26 to 30 of the invention, it is understood that the pH control with the pH-controlling agent is effective for improving the properties of the powder magnetic core, especially for increasing the specific resistance thereof.

[0092] Pressing only the starting powder formed comparative samples 1 and 2. Not coated with the coating material, the specific resistivity of these comparative samples was extremely low.

[0093] For comparative samples 3 to 5, the starting powder was coated with water-dispersible epoxy resin (resin concentration, 5 mass %) but not with the coating material of the invention. These comparative samples were fabricated and evaluated in the same manner as that for the samples of the invention. The magnetic flux density of the epoxy resin-coated samples was much lower than that of the samples of the invention that had been fabricated by coating the starting powder with the same amount of the coating material followed by pressing the coated powder under the same pressure.

[0094] For comparative sample 6, the starting powder was mixed with a predetermined amount of 0.1 N sulfuric acid; and for comparative sample 7, it was mixed with a predetermined amount 85 % orthophosphoric acid. The resulting metal powder was dried and evaluated in the same manner as that for the samples of the invention. It is understood that the insulation performance and the magnetic properties of these comparative samples worsened in time.

[0095] For comparative samples 8 and 9, the starting powder was processed with an aqueous solution that had been prepared by dissolving 163 g of 85 % orthophosphoric acid, 31 g of MgO and 30 g of boric acid in one liter of distilled water followed by

further adding distilled water thereto to make it have a solid concentration of 5 % by mass, in the same manner as that for the samples of the invention, and the resulting samples were evaluated also in the same manner as the samples of the invention. It is understood that the specific resistivity of these comparative samples is much lower than that of samples 18 and 19 of the invention for which the starting powder was coated with the same amount of the coating material of the invention and was pressed under the same molding pressure.

[0096] For comparative sample 10, the starting powder was coated with water-dispersible amide resin (solid concentration, 5 mass %). The coated powder was pressed and then heated at 200°C for 2 hours, and the thus-pressed sample was evaluated. It is understood that the specific resistivity of the sample is high but the magnetic flux density thereof is extremely low.

#### **Example 2:**

[0097] Ring samples (outer diameter, 38 mm; inner diameter, 25 mm; height, 6.2 mm) were fabricated in the same manner as in Example 1, for which, however, the ratio P/M and the value  $\alpha$  of the coating material were changed as in Table 3 below.

[0098] The green density, the specific resistivity and the magnetic flux density of these samples were measured, and the data are given in Table 4.



Table 3

No.	Coating Material											Remarks	
	Phosphoric Acid Compound	Metal Compound I		Metal Compound II			P/M	$\alpha$	pH	Coating Condition			Molding Condition
		designation	ratio*	designation	ratio*	designation				ratio*	Solid Content (mas.%)		
41	orthophosphoric acid	aluminum phosphate				0	1	1	1.3	1.0	980	sample 31 of the invention	
42	orthophosphoric acid	aluminum phosphate	100	-		0	2	1	1.2	1.0	980	sample 32 of the invention	
43	orthophosphoric acid	aluminum phosphate	100	-		0	3	1	1.2	1.0	980	sample 33 of the invention	
44	orthophosphoric acid	aluminum phosphate	100	-		0	4	1	1.0	1.0	980	sample 34 of the invention	
45	orthophosphoric acid	aluminum phosphate	100	-		0	10	1	1.0	1.0	980	sample 35 of the invention	
46	orthophosphoric acid (85 %)	aluminum hydroxide	30	zinc phosphate		70	3	0.3	1.2	0.5	1470	sample 36 of the invention	
47	orthophosphoric acid (85 %)	aluminum hydroxide	50	zinc phosphate		50	3	0.5	1.2	0.5	1470	sample 37 of the invention	
48	orthophosphoric acid (85 %)	aluminum hydroxide	80	manganese phosphate		20	3	0.8	1.2	0.5	1470	sample 38 of the invention	
49	orthophosphoric acid (85 %)	aluminum hydroxide	90	manganese phosphate		10	3	0.9	1.2	0.5	1470	sample 39 of the invention	
50	orthophosphoric acid (85 %)	aluminum hydroxide	100	-		0	3	1	1.2	0.5	1470	sample 40 of the invention	

\* Ratio: This is the ratio of the metal element atom of the indicated component to the number of atoms M of all the metal components.

Table 4

No.	Condition in Sample Preparation					immediately after preparation			after 10 days		Remarks
	$\alpha$	P/M	solid content (mas.%)	Molding Pressure (MPa)	Heat Treatment	Green Density (Mg/m <sup>3</sup> )	Specific resistivity ( $\mu\Omega$ m)	Magnetic Flux Density B10k (T)	Specific resistivity ( $\mu\Omega$ m)	Magnetic Flux Density B10k (T)	
41	1	1	1	980	yes	7.45	120	1.49	120	1.49	sample 31 of the invention
42	1	2	1	980	yes	7.46	898	1.48	899	1.49	sample 32 of the invention
43	1	3	1	980	yes	7.44	1251	1.47	1249	1.48	sample 33 of the invention
44	1	4	1	980	yes	7.45	450	1.47	451	1.44	sample 34 of the invention
45	1	10	1	980	yes	7.45	232	1.48	210	1.43	sample 35 of the invention
46	0.3	3	0.5	1470	yes	7.59	120	1.56	121	1.45	sample 36 of the invention
47	0.5	3	0.5	1470	yes	7.62	232	1.54	235	1.49	sample 37 of the invention
48	0.8	3	0.5	1470	yes	7.64	380	1.59	382	1.59	sample 38 of the invention
49	0.9	3	0.5	1470	yes	7.64	376	1.59	394	1.60	sample 39 of the invention
50	1	3	0.5	1470	yes	7.65	385	1.59	384	1.60	sample 40 of the invention

[0099] Table 4 confirms the following. Comparing samples 31 to 35 of the invention with each other, it is understood that, when the ratio P/M falls between 2 and 3, then the insulation performance of the samples is good and, in addition, the properties of the samples stored for 10 days fluctuate little and are stable. Comparing samples 36 to 40 of the invention with each other, it is understood that, when the molar fraction,  $\alpha$ , of aluminum is closer to 1, then the insulation performance of the samples is better and, in addition, the properties of the samples stored for 10 days fluctuate little and are stable.

**Example 3:**

[0100] Iron powder KIP-304AS (by JFE Steel) was used for the starting powder. For the coating material, the phosphoric acid compound that had been conditioned to have a ratio P/M and a value  $\alpha$  as in Table 5 below was used. For the ratio P/M, the data were rounded off.

[0101] The powder was coated in wet treatment. The solution for the wet treatment had a solid concentration of 5 % by mass in distilled water.

[0102] The ratio P/M was controlled in the same manner as in Example 1.

[0103] For coating the starting iron powder with the coating material, the powder was stirred in a Henschel mixer and a solution of the coating material was sprayed on the powder being stirred in the mixer. The amount of the coating material sprayed on the powder was as in Table 5, in terms of the solid content of the coating material. During the coating treatment, the temperature of the starting powder and the coated powder was 80°C. The coated powder was dried in air at room temperature for 24 hours.

[0104] Next, the powder was processed in different methods as shown in Table 5 for making it resistant to moisture absorption. Concretely, the treatment for moisture

absorption resistance was effected after the coating treatment with the phosphate. This is as follows. An aqueous solution of the moisture-resistant material having a solid concentration of 5 % by mass was sprayed on the powder in a Henschel mixer in the same manner as that for spraying the phosphate on it. Thus sprayed, the powder was dried in air at room temperature for 24 hours. On the other hand, the powder was coated with a single substance of oxide sol having a mean particle size of 50 nm. Apart from these, the treatment with the phosphate and the treatment with the moisture-resistant material were similar and explained below. The moisture-resistant material was added to the phosphate solution and was processed to have a solid concentration of 5 % by mass. The resulting solution was then applied to the starting powder.

[0105] Thus prepared, the powder was exposed to a temperature of 20°C and a relative humidity of 30 % for 1 day and for 60 days.

[0106] Each sample was molded into ring samples in the same manner as in Example 1, and the green density, the specific resistivity and the magnetic flux density of each ring sample was measured. The resulting data is shown in Table 6.

[0107] Mold lubrication was used during molding of the samples. Some of the molded samples were subjected to heat treatment as shown in Table 6, for which the heat treatment condition was the same as in the condition of Example 1.

[0108] HLB in Table 5 is an abbreviation of "hydrophile lipophile balance", and indicates the degree of hydrophilicity (that is, the solubility in water) of the nonionic surfactant.

Table 5

No.	Phosphoric Acid Compound	P/M	$\alpha$	Solid Content (mas. %)	Treatment for Moisture Absorption Resistance			Remarks
	Designation				mode of treatment	condition for treatment	amount added (mas. %)	
1	aluminum phosphate	3	1	0.20	not treated	-	-	sample 41 of the invention
2	aluminum phosphate	3	1	1.00	not treated	-	-	sample 42 of the invention
3	aluminum phosphate	3	1	0.20	powder heating	Heated in air at 150°C for 30 min.	-	sample 43 of the invention
4	aluminum phosphate	3	1	1.00	powder heating	Heated in air at 250°C for 30 min.	-	sample 44 of the invention
5	aluminum phosphate	3	1	0.20	coating with oxide	Coated with aluminum phosphate and then further with colloidal silica.	0.1	sample 45 of the invention
6	aluminum phosphate	3	1	1.00	mixing with oxide	Aluminum phosphate was mixed with zirconia sol, and the resulting mixture was used for simultaneous coating treatment and moisture resistance treatment.	0.5	sample 46 of the invention
7	aluminum phosphate	3	1	0.20	coating with oxide	Coated with aluminum phosphate and then further with ethyl silicate.	0.1	sample 447 of the invention
8	aluminum phosphate	3	1	1.00	coating with resin	Coated with aluminum phosphate and then further with silicone resin.	0.5	sample 48 of the invention
9	aluminum phosphate	3	1	0.20	mixing with surfactant	Aluminum phosphate was mixed with nonionic surfactant (polyoxyethylene alkyl ether with HLB of 13.6), and the resulting mixture was used for simultaneous coating treatment and moisture resistance treatment.	0.05	sample 49 of the invention

No.	Phosphoric Acid Compound designation	P/M	$\alpha$	Solid Content (mas. %)	Treatment for mode of treatment	Moisture Absorption Resistance condition for treatment	amount added (mas. %)	Remarks
10	aluminum phosphate	3	1	0.20	coating with surfactant	Coated with aluminum phosphate and then further with ionic surfactant (polyoxyethylene alkylamine).	0.05	sample 50 of the invention
11	aluminum phosphate	3	1	0.20	mixing with silane	Coated with aluminum phosphate and then further with alkylsilane (trimethylmethoxysilane).	0.02	sample 51 of the invention
12	aluminum phosphate	3	1	0.20	coating with silane	Coated with aluminum phosphate and then further with aminosilane (aminopropyltriethoxysilane).	0.02	sample 52 of the invention
13	aluminum phosphate	3	1	1.00	coating with silane	Coated with aluminum phosphate and then further with alkoxysilane (trimethylmethoxysilane).	0.05	sample 53 of the invention
14	aluminum phosphate	3	1	0.20	coating with silane	Coated with aluminum phosphate and then further with aminosilane (aminopropyltriethoxysilane).	0.02	sample 54 of the invention
15	aluminum phosphate zinc phosphate orthophosphoric acid	3	0.9	0.50	coating with silane	Coated with aluminum phosphate and then further with aminosilane (aminopropyltriethoxysilane).	0.02	sample 55 of the invention

Table 6

No.	P/M	Amount Added (mas.%)	Molding Pressure (MPa)	Heat Treatment	Specific Resistivity ( $\mu\Omega\text{m}$ )		Green Density ( $\text{Mg/m}^3$ )		Magnetic Flux Density B10k (T)		Remarks
					after 1-day exposure	after 60-day exposure	after 1-day exposure	after 60-day exposure	after 1-day exposure	after 60-day exposure	
1	3	0.20	1470	no	451	915	7.62	7.62	1.65	1.66	sample 41 of the invention
2	3	1.00	1470	no	3250	6580	7.54	7.54	1.53	1.54	sample 42 of the invention
3	3	0.20	1470	no	320	500	7.63	7.62	1.64	1.66	sample 43 of the invention
4	3	1.00	1470	no	1754	2201	7.55	7.54	1.54	1.53	sample 44 of the invention
5	3	0.20	1470	no	870	865	7.50	7.49	1.50	1.51	sample 45 of the invention
6	3	1.00	1470	no	3545	3812	7.43	7.44	1.46	1.49	sample 46 of the invention
7	3	0.20	1470	no	890	882	7.53	7.54	1.53	1.53	sample 447 of the invention
8	3	1.00	1470	no	3545	3987	7.43	7.44	1.48	1.49	sample 48 of the invention
9	3	0.20	1470	no	556	670	7.60	7.61	1.65	1.64	sample 49 of the invention
10	3	0.20	1470	no	601	615	7.61	7.62	1.65	1.65	sample 50 of the invention
11	3	0.20	1470	no	870	910	7.62	7.62	1.66	1.65	sample 51 of the invention
12	3	0.20	1470	no	901	900	7.62	7.63	1.65	1.66	sample 52 of the invention
13	3	1.00	1470	no	3650	3648	7.54	7.55	1.53	1.53	sample 53 of the invention

14	3	0.20	1470	yes	405	410	7.62	7.62	1.65	1.65	sample 54 of the invention
15	3	0.50	1980	yes	450	455	7.60	7.61	1.64	1.64	sample 55 of the invention



[0109] From Table 6 above, it is understood that samples 43 to 53 of the invention that had been treated for moisture absorption resistance fluctuated little in point of the specific resistivity thereof and were stable even after subjected to 60-day exposure. Comparing samples 43 and 44 of the invention with samples 45 to 53 of the invention, it is understood that the moisture resistance treatment effected by coating the powder with the moisture-resistance material is more effective than that effected by heating the powder in that the specific resistance of the samples treated by the former mode is more stable than that of the samples treated by the latter mode.

[0110] Samples 49 to 53 of the invention that had been treated with surfactant or silane are better than samples 45 to 48 of the invention that had been treated with oxide or resin in that the green density and the magnetic flux density of the former are higher than those of the latter. This confirms that surfactant and silane are more suitable to the moisture-resistant material for use in the invention. When sample 49 of the invention that was coated with surfactant and phosphate compound at the same time is compared with sample 50 of the invention that was separately coated with them, it is understood that the specific resistivity of the latter is more stable than that of the former. This confirms that separately coating the powder is more effective for moisture absorption resistance.

[0111] Samples 52 and 53 of the invention processed with aminosilane are better than the other samples in that their specific resistance is much more stable than that of the others. This confirms that aminosilane is extremely effective for the treatment for moisture absorption resistance.

[0112] Sample 54 of the invention was fabricated in the same manner as that for sample 52 of the invention, and this was further subjected to heat treatment. Thus processed, sample 54 also enjoyed the same effect as that of the others.

[0113] Except samples 41 and 42 of the invention not processed for moisture absorption resistance, all the samples of the invention had good powder flowability even after 60-day exposure.

**Example 4:**

[0114] Sendust powder having a mean particle size of 80  $\mu\text{m}$ , iron-based cobalt alloy amorphous powder, 4 % Mo-79 % Ni permalloy powder, and Fe-3 % Si alloyed powder was prepared. In the same manner as in Example 1, these were coated with the coating material as in Table 7, in which the ratio P/M and the value  $\alpha$  are given, and the coated powder were molded into ring samples (outer diameter, 38 mm; inner diameter, 25 mm; height, 6.2 mm).

[0115] The green density, the specific resistivity and the magnetic flux density of the thus-obtained ring samples were measured, and the data are given in Table 8.

[0116] This confirms the effectiveness of the invention not only for iron powder but also for other metal and alloyed powders.

Table 7

No.	Coating Material						Coating Condition				Molding Condition	Remarks
	Phosphoric Acid Compound	Metal Compound I		Metal Compound II			P/M	$\alpha$	pH	Solid Content (mas. %)		
		designation	ratio*	designation	ratio*							
51	orthophosphoric acid	aluminum phosphate	100	-	0	3	1	1.2	1.0	980	sample 31 of the invention, sendust powder used	
52	orthophosphoric acid	aluminum phosphate	100	-	0	3	1	1.2	1.0	980	sample 32 of the invention, amorphous powder used	
53	orthophosphoric acid	aluminum phosphate	100	-	0	3	1	1.2	1.0	980	sample 33 of the invention, permalloyed powder used	
54	orthophosphoric acid	aluminum phosphate	100	-	0	3	1	1.2	1.0	980	sample 34 of the invention, Fe-3 % Si powder used	

\* Ratio: This is the ratio of the metal element atom of the indicated component to the number of atoms M of all the metal components.

Table 8

No.	Condition in Sample Preparation					immediately after preparation				after 10 days		Remarks
	$\alpha$	P/M	solid content (mas.%)	Molding Pressure (MPa)	Heat Treatment	Green Density (Mg/m <sup>3</sup> )	Specific resistivity ( $\mu\Omega\text{m}$ )	Magnetic Flux Density B10k (T)	Specific resistivity ( $\mu\Omega\text{m}$ )	Magnetic Flux Density B10k (T)		
51	1	2	1	980	yes	5.70	25467	0.89	26450	0.89	sample 41 of the invention	
52	1	2	1	980	yes	7.20	12476	1.30	12456	1.31	sample 42 of the invention	
53	1	2	1	980	yes	7.44	69825	0.58	70487	0.59	sample 43 of the invention	
54	1	2	1	980	yes	7.21	5467	1.35	5456	1.35	sample 44 of the invention	

**Example 5:**

[0117] Iron powder KIP-304AS (by JFE Steel) was used for the starting powder. For the coating material, the phosphoric acid compound and the metal compound that had been conditioned to have a ratio P/M as in Table 9 below, were used. For the ratio P/M, the data was rounded off. The molar ratio,  $\alpha$ , of aluminum to M is also shown in Table 9.

[0118] Using a Henschel mixer and a spray, the starting powder was coated with the phosphoric acid compound in the same manner as in Example 3. The temperature of the starting powder and the coated powder is shown in Table 9. The coated powder was dried in air at room temperature for 24 hours.

[0119] Next, some samples were treated for moisture absorption resistance according to the method shown in Table 9. Concretely, the treatment for moisture absorption resistance was effected after the coating treatment with the phosphate compound. This is as follows. An aqueous solution of the moisture-resistant material having a solid concentration of 5 % by mass was sprayed on the powder in a Henschel mixer in the same manner as that for spraying the phosphate compound on it. Thus sprayed, the powder was dried in air at room temperature for 24 hours. Apart from it, the treatment with the phosphate compound and the treatment with the moisture-resistant material were effected at the same. This is as follows. The moisture-resistant material was added to the phosphate solution and this was processed to have a solid concentration of 5 % by mass. The resulting solution was applied to the starting powder.

[0120] Thus prepared, the powder was exposed to a temperature of 20°C and a relative humidity of 30 % for 1 day and for 60 days. Each sample was molded in a mold into ring samples (outer diameter, 38 mm; inner diameter, 25 mm; height, 6.2 mm). The molding pressure fell between 686 and 1980 MPa. Applying a lubricant dispersion,

which had been prepared by dispersing zinc stearate in water, to the inner wall thereof, lubricated the mold. The molded samples were heated in air at 400°C for 60 minutes. The molding pressure is shown in Table 9.

[0121] The green density, the specific resistivity and the magnetic flux density of the thus-molded ring samples were measured, and the data are given in Table 10. The size and the weight of each sample were measured, and the green density thereof was computed from the data. The specific resistivity was measured according to a four-terminal method in which the current was 1 A. The magnetic flux density was measured as follows. A formal wire of 0.6 mm in diameter was wound around the ring sample, with 100 turns on the primary side and 20 turns on the secondary side. The resulting coil was tested for the magnetic flux density  $B_{10k}$  thereof in a magnetic field  $H = 10$  kA/m.

[0122] Comparing samples 45 to 64 of the invention with samples 65 to 67 of the invention, it is obvious that the insulation performance of the molded samples is extremely good when the coating temperature is lower than 110°C. Comparing samples 47 to 49 of the invention with each other, it is understood that the insulation performance of the samples is good when the coating temperature is not higher than 100°C, and the insulation performance thereof is better when the coating temperature is not higher than 90°C. From samples 63 and 64 of the invention, it is understood that, when the coating temperature of lower than 110°C is combined with the treatment for moisture absorption resistance, then the samples are more stable with no fluctuation of their properties even after being stored for 60 days. Comparing samples 51 to 53 with each other, it is understood that, when the ratio  $P/M$  is set between 2 and 3, then the specific resistivity and the magnetic flux density of the samples are more stable with little fluctuation thereof even after 60-day exposure. Comparing samples 59 to 62 with

each other, it is understood that, when the molar fraction,  $\alpha$ , of aluminum is nearer to 1, then the properties of the samples are more stable with little fluctuation thereof even after 60-day exposure. 0.5 % by mass of zinc stearate powder was added to the powder for sample 48 of the invention, and the resulting mixture was pressed to prepare a sample, and this was evaluated. In molding the mixture therein, the mold was not lubricated. The sample of this case was also good, like sample 48 of the invention.

Table 9

No.	Coating Material			Coating Condition					Treatment for Moisture Absorption Resistance				Molding Condition	Remarks
	phosphoric acid compound	metal compound I	metal compound II	$\alpha$	P/M	pH	solid content (mas. %)	coating temperature (°C)	mode of treatment	condition for treatment	amount added (mas. %)	molding pressure (MPa)		
55	orthophosphoric acid (85 %)	aluminum acetate	-	1	3	1.2	0.01	60	not treated	-	-	980	sample 45 of the invention	
56	orthophosphoric acid (85 %)	aluminum acetate	-	1	3	1.2	0.05	90	not treated	-	-	1980	sample 46 of the invention	
57	-	aluminum phosphate	-	1	3	1.2	0.2	105	not treated	-	-	980	sample 47 of the invention	
58	-	aluminum phosphate	-	1	3	1.2	0.2	95	not treated	-	-	980	sample 48 of the invention	
59	-	aluminum phosphate	-	1	3	1.2	0.2	90	not treated	-	-	980	sample 49 of the invention	
60	-	aluminum phosphate	-	1	3	1.2	0.5	105	not treated	-	-	1470	sample 50 of the invention	
61	-	aluminum phosphate	-	1	1	1.2	1.0	100	not treated	-	-	1980	sample 51 of the invention	
62	orthophosphoric acid (85 %)	aluminum phosphate	-	1	3	1.2	1.0	100	not treated	-	-	1980	sample 52 of the invention	
63	orthophosphoric acid (85 %)	aluminum phosphate	-	1	5	1.2	1.0	100	not treated	-	-	1980	sample 53 of the invention	
64	orthophosphoric acid (85 %)	aluminum phosphate	-	1	3	1.2	2.0	90	not treated	-	-	1176	sample 54 of the invention	
65	orthophosphoric acid (85 %)	aluminum hydroxide	-	1	3	1.2	0.5	80	not treated	-	-	1470	sample 55 of the invention	
66	orthophosphoric acid (85 %)	aluminum hydroxide	-	1	4	1.2	0.5	100	not treated	-	-	1470	sample 56 of the invention	
67	orthophosphoric acid (85 %)	aluminum acetate	-	1	1	1.2	2.0	60	not treated	-	-	1176	sample 57 of the invention	
68	orthophosphoric acid (85 %)	aluminum hydroxide	boric acid	1	6	1.0	5.0	90	not treated	-	-	686	sample 58 of the invention	
69	orthophosphoric acid (85 %)	aluminum hydroxide	manganese phosphate	0.1	10	1.0	3.0	80	not treated	-	-	686	sample 59 of the invention	



No.	Coating Material						Coating Condition		Treatment for Moisture Absorption Resistance			Molding Condition	Remarks
	phosphoric acid compound	metal compound I	metal compound II	$\alpha$	P/M	pH	solid content (mas. %)	coating temperature (°C)	mode of treatment	condition for treatment	amount added (mas. %)	molding pressure (MPa)	
70	orthophosphoric acid (85 %)	aluminum hydroxide	manganese phosphate	0.4	10	1.0	3.0	80	not treated	-	-	686	sample 60 of the invention
71	orthophosphoric acid (85 %)	aluminum hydroxide	manganese phosphate	0.8	10	1.0	3.0	80	not treated	-	-	686	sample 61 of the invention
72	orthophosphoric acid (85 %)	aluminum hydroxide	-	1	10	1.0	3.0	80	not treated	-	-	686	sample 62 of the invention
73	-	aluminum phosphate	-	1	3	1.2	0.1	80	surfactant added	Phosphoric acid compound II was mixed with nonionic surfactant (polyoxyethylene alkyl ether with HLB of 13.6), and the resulting mixture was used for simultaneous coating treatment and moisture resistance treatment.	0.05	980	sample 63 of the invention
74	-	aluminum phosphate	-	1	3	1.2	0.5	80	coated with silane	Coated with phosphoric acid compound and then further with aminosilane (aminopropyl-triethoxysilane).	0.05	980	sample 64 of the invention

No	Coating Material						Coating Condition		Treatment for Moisture Absorption Resistance			Molding Condition	Remarks
	phosphoric acid compound	metal compound I	metal compound II	$\alpha$	P/M	pH	mode of treatment	condition for treatment	mode of treatment	condition for treatment	amount added (mas. %)	molding pressure (MPa)	
75	orthophosphoric acid (85 %)	aluminum hydroxide	-	1	4	1.2	0.5	150	not treated	-	-	1470	sample 65 of the invention
76	orthophosphoric acid (85 %)	aluminum hydroxide	manganese phosphate	0.8	10	1.0	3.0	180	not treated	-	-	686	sample 66 of the invention
77	-	aluminum phosphate	-	1	3	1.2	0.5	110	coated with silane	Coated with phosphoric acid compound and then further with aminosilane (aminopropyl-triethoxysilane)	0.05	980	sample 67 of the invention

Table 10

No.	Condition for Sample Preparation					Properties of Sample after 1-day exposure				Properties of Sample after 60-day exposure				Remarks
	$\alpha$	P/M	solid content (mas.%)	coating temperature (°C)	molding pressure (MPa)	green density (Mg/m <sup>3</sup> )	specific resistivity (μΩm)	magnetic flux density B10k (T)	green density (Mg/m <sup>3</sup> )	specific resistivity (μΩm)	magnetic flux density B10k (T)	magnetic flux density B10k (T)		
55	1	3	0.01	60	980	7.65	21	1.70	7.65	35		1.71	sample 45 of the invention	
56	1	3	0.05	90	1980	7.70	41	1.74	7.69	68		1.74	sample 46 of the invention	
57	1	3	0.2	105	980	7.62	200	1.64	7.63	268		1.64	sample 47 of the invention	
58	1	3	0.2	95	980	7.63	312	1.65	7.62	452		1.64	sample 48 of the invention	
59	1	3	0.2	90	980	7.62	1214	1.64	7.62	1542		1.63	sample 49 of the invention	
60	1	3	0.5	105	1470	7.60	540	1.61	7.60	701		1.61	sample 50 of the invention	
61	1	1	1.0	100	1980	7.63	1420	1.62	7.63	1790		1.58	sample 51 of the invention	
62	1	3	1.0	100	1980	7.64	2543	1.61	7.64	3521		1.60	sample 52 of the invention	
63	1	5	1.0	100	1980	7.64	850	1.63	7.62	1250		1.58	sample 53 of the invention	
64	1	3	2.0	90	1176	7.50	3545	1.50	7.51	4554		1.52	sample 54 of the invention	
65	1	3	0.5	80	1470	7.60	1350	1.66	7.61	1875		1.65	sample 55 of the invention	
66	1	4	0.5	100	1470	7.58	102	1.60	7.57	125		1.61	sample 56 of the invention	
67	1	1	2.0	60	1176	7.51	1545	1.51	7.52	1875		1.50	sample 57 of the invention	
68	1	6	5.0	90	686	7.20	15424	1.21	7.20	16584		1.21	sample 58 of the invention	
69	0.1	10	3.0	80	686	7.12	8542	1.15	7.10	15487		1.10	sample 59 of the invention	
70	0.4	10	3.0	80	686	7.12	9781	1.16	7.11	14871		1.15	sample 60 of the invention	

No.	Condition for Sample Preparation					Properties of Sample after 1-day exposure			Properties of Sample after 60-day exposure			Remarks
	$\alpha$	P/M	solid content (mas.%)	coating temperature (°C)	molding pressure (MPa)	green density (Mg/m <sup>3</sup> )	specific resistivity ( $\mu\Omega\text{m}$ )	magnetic flux density B10k (T)	green density (Mg/m <sup>3</sup> )	specific resistivity ( $\mu\Omega\text{m}$ )	magnetic flux density B10k (T)	
71	0.8	10	3.0	80	686	7.12	10541	1.15	7.12	13540	1.15	sample 61 of the invention
72	1	10	3.0	80	686	7.12	12455	1.15	7.11	13154	1.16	sample 62 of the invention
73	1	3	0.1	80	980	7.64	1542	1.65	7.64	1610	1.65	sample 63 of the invention
74	1	3	0.5	80	980	7.61	3546	1.60	7.61	3601	1.61	sample 64 of the invention
75	1	4	0.5	150	1470	7.61	62	1.61	7.61	54	1.51	sample 65 of the invention
76	0.8	10	3.0	180	686	7.11	2130	1.21	7.10	2100	1.15	sample 66 of the invention
77	1	3	0.5	110	980	7.61	1570	1.60	7.60	1210	1.51	sample 67 of the invention